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PROPERTIES OF NEW SUPERCONDUCTING MATERIALS

by

Professor T. H. Geballe Principal Investigator

Department of Applied Physics Stanford University Stanford, California 94305

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A large number of new and unusual superconductors have been discovered and their superconducting response to changes effected chemically, crystallographically and physically has been studied. In this way, the interactions giving rise to superconductivity were examined. The effort has been concentrated in two major areas. First, the two-dimensionality of layered transition metal dichalcogenides has allowed for a closer comparison between theory and experiment. Second, studying the instabilities of the high transition temperature phases has led to a greater understanding of the role of crystal structure and stoichiometry.

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During the period of the grant and its predecessor an entirely new class of superconductors - the intercalated layered transition metal dichalcogenides - was discovered and investigated. More than 75 new superconducting crystals of this class have been synthesized in collaboration with the industry-supported group of F. R. Gamble and associates. This probably represents most of the new superconductors discovered during the past 10 years.

The distinguishing feature of these intercalated superconductors is that there are easily identifiable dichalcogenide layers in which the conduction takes place. These superconductors are the most anisotropic compounds known. The conductivity in the approximately 6 angstrom thick dichalcogenide layer was found to be that of a typical metallic alloy. The rest of the unit cell of the crystal is formed by an organic insulating layer which, in the case of octadecylalamine is 50 angstroms thick. Electrical anisotropies of greater than 105 have been found at room temperature for some of the more perfect crystals. The anisotropic Ginzburg-Landau parameters in 20 different single crystal superconductors were investigated using newly developed heat capacity methods as well as electrically. The coherence length in TaS1.6Se1.4(C6H5N) was found to be only 4.5 angstroms in the direction perpendicular to the layers (vs 220 angstroms parallel to the layers). The perpendicular distance is less than the interlayer separation of the conducting dichalcogenide layers demonstrating that the magnetic field can pass through the superconductor without inducing large diamagnetic screening currents. As a consequence, the upper critical field (measured parallel to the surface) was found to increase at the record rate of > 140,000 gauss per degree as the sample was cooled below its transition.

Using new electrolytic methods of intercalations, the stoichiometric compound $-TaS_2(H_2N-CH_2-CH_2-NH_2)_{1/4}$ was formed upon intercalation of

monocrystalline 4H(b)-TaS2 (a polymorph of TaS2 with four layers per unit cell), with ethylenediamine. In contrast to $4H(b)-TaS_2$ ($T_c < 0.5K$), the intercalated compounds were found by heat capacity measurements (1) to undergo a bulk superconducting transition near 3 K, (2) to have a marked increase in its electronic density of states and (3) to show the intriguing possibility of being a superconductor with no energy gap. The transition temperature was also raised to about 3 K in 4Hb-TaS, by intercalation of hydrogen apparently because of hydrogen's role in suppressing the charge density waves. The latter are instabilities driven by the Fermi-surface. Thermal and electrical properties in the hexagonal polymorphs of NbSe, , ${\tt TaS}_2$, ${\tt TaSe}_2$, and the mixed trigonal and hexagonal polymorphs of ${\tt TaS}_2$ and TaSe, were measured and interpreted in terms of a model in which only a small fraction of the Fermi surface participates in the formation of the charge density wave. A systematic study of the optical properties in a series of crystals in the lT(Ti_{1-x}Ta_xS₂) system has suggested why these compounds behave electrically as semiconductors on the Ta-rich side rather than as the superconductors one would expect. Analysis of their Drude-like optical behavior shows that scattering times become remarkably short for the tantulum rich compounds $(x \ge 0.6)$, so short in fact that the Boltzmann transport equation no longer applies. An unexpected quadratic dependence of resistivity upon temperature was found over a wide range in TiS, suggesting electron-hole scattering as the mechanism.

B. W. Roberts in "Survey of Superconductive Materials and Critical Evaluation of Selected Properties", has tabulated in Table III, a copy of which is appended, the properties of superconducting materials with organic and related constituents. References 1128 and 1192 in particular refer to research discussed above. This important work has resulted in widespread national and international recognition and has directly stimulated new

research in other laboratories. A special conference was sponsored by
the ONR, "Physics and Chemistry of Layered Compounds", Monterey, California,
August 1972, a Gordon Research Conference has been held "Chemistry and Physics
of Solids", Holderness School, Plymouth, N.H., August 1975, and an international conference, "Layered Semiconductors and Metals", a Satellite
Conference of I.C.P.S., has been held in Bari, Italy, September 1976. An
active group has developed at the University of Illinois under F. C. Brown,
W. M. McMillan, and others. Work in the high magnetic field properties
and superconductive fluctuations at high temperatures was undertaken by
M. R. Beasley, A. H. Luther and R. A. Klemm at Harvard and has been continued by
D. Prober at Yale. Important charge density wave instabilities were
discovered at Bell Laboratories by F. J. DiSalvo, J. R. Wilson and
S. Mahajan. More indirectly linked research on the mechanism of the
intercalation reaction has resulted in promising new battery electrodes
by workers at Exxon and Bell.

During the latter part of the grant an improved method of growing high temperature A-15 compounds was developed using the method of electron beam codeposition. Elements were evaporated from individually controlled electron beam sources exploiting a method of fast feedback developed in this laboratory. The phase diagram of Nb₃Ge below 1000 K was investigated and showed that the Ge-rich boundary extends beyond the 20-22 at % previously established and exhibits an unusual temperature dependence when trace gases such as 0₂ and Cl₂ are present in the evaporator at partial pressures of 10⁻⁵ - 10⁻⁶ torr. A careful investigation of Nb₃Ge showed no evidence for a low-temperature martensitic transformation such as that found in Nb₃Sn . A potentially very powerful new method, "polycrystalline" epitaxy, which in some sense is equivalent to molecular beam epitaxy, was developed for synthesizing metastable compounds. Using this method the Ge-rich phase

boundary of Nb₃Ge was extended from the thermodynamic limit of 19 atomic percent to 26 at %. Either Nb₃Ir or Nb₃Rh pre-evaporated as a polycrystalline substrate was found to be effective since both have suitable lattice constants. The resulting Nb₃Ge films were found to have superconducting transition temperatures which maximize, at the stoichiometric composition, with temperatures in excess of 22 K. Another consequence of this electron beam technology was the development of a method to produce oxide tunnel junctions of Nb₃Sn in which parameters such as composition could be varied systematically for the first time.

New approaches have been opened for the synthesis of stoichiometric compositions of other A-15 compounds for which the thermodynamic limit of the B element is less than 25% such as Nb₃Al and Nb₃Ga. By analogy with what has been found for Nb₃Ge the superconducting transitions should be above the present values of 18.8 K and 20.7 K respectively. The possibility of making Nb₃Si stable in the A-15 phase by epitaxial means has also been opened, and here the transition temperature is expected to exceed the highest present day value of 23 K.

There were other significant developments in this 5 year period including a new method of introducing hydrogen into palladium electrolytically from methanol at - 80 C which resulted in stoichiometric PdH with T_c = 9.1 K. This method has been adopted by other research groups both in the US and abroad. A relationship was established between hydrogen concentration and the resistivity maxima observed at temperatures above T_c due to clustering of the hydrogen. The prototype of a possible new class of metallic compounds was found in collaboration with C. W. Chu, visiting from Cleveland State, and A. P. Rusakov, a Russian visitor at Stanford under an exchange program.

CuCl was found to transform into a highly-conducting state over a relatively narrow pressure range above 40 Kbar. The new phase occurred as an intermediate between the low pressure (cubic) and high pressure (rock-salt) phases both of which are insulators. Further research has been carried out by both Dr. C. W. Chu, now at University of Houston, and Dr. Rusakov in Moscow.

TABLE 3. Properties of Superconductive Materials with Organic and Related Constituents NOTE: "HF" Signifies high-magnetic-field data in Table 5.

Material	T _c (K)	H _o (oersted)	Crystal Structure	T _n (K)	Refs.
Al(and tetracyanoquino- dimethan)	2.7-5.24 1.9-3.7(annealed)				∇1078
Be(with KCl layers; deposit 4.2K)	10.6-6.5				V1028
Be(with zinc-etioporphyrin; deposit 4.2K; ≥ 500 Å)	10.2				▼1028
CaH ₁₈ N _G				1.9	010
H ₁₂ LiN ₄				1.9	010
In (with Anthraquinone, 5000Å)	3.4-4.6				V1076 ∇1528
MoS2Ba0.2(NH3)x	5.7		HEX		1918
MoS ₂ Ca _{0,2} (NH ₃) _x	3.6		HEX		1918
MoS ₂ Sr _{0.01-1} (NH ₃) _{0.01-1.62}	5.2-4.9				1918
MoS2Yb0.1(NH3)0.16	2.4		HEX		1918
MoSe ₂ Sr _{0,2} (NH ₃) _x	5.0		HEX		1918
NS	0.26				1986 1975#
NbS ₂ (Ammonia)	2.0		HEX		1192
NbS ₂ (Aniline) ₂	4.0		HEX		1192
NbS ₂ (S-collidine) _{0.17}	3.5		HEX		1192
NbS ₂ (pyridine) _{0.5}	4.0		HEX		1192 1027
NbS ₂ (tributylphosphine) _{0,125}	3.5		HEX		1192
Nb3Sn (with CO2, CO, CH3,		HF			1169 1168
N2, O2, ammonium,					₹1437
boron tricloride, ethane, hydrogen sulfide, nitrogen oxide, propane)		•			
PdTe ₂ (pyridine) _{0.5}	1.65				1027
S2-1Se0-1Ta (pyridine)0.5	0,8-3,3-1,6		HEX		1910
S SeTa (pyridine)	1.5	HF	HEX		1262
S2Ta (2-aminopyridine)0.53	3.25		HEX		1128
S2Ta (4-aminopyridine)0.51	3.4		HEX		1128
S ₂ Ta (ammonía)	4.2		HEX		1192
S2Ta (ammonium acetate)	2.0		HEX ,		1192
S2Ta (ammonium hydroxide)	3.3		HEX		1192
S2Ta (amylamine)	2.2				1192
S2Ta (aniline)	3, 1		HEX		1192
S2Ta (aniline)0.75	3,1		HEX		1192

TABLE 3 (Cont'd). Properties of Superconductive Materials with Organic and Related Constituents NOTE: "HF" Signifies high-magnetic-field data in Table 5.

Material	T _c (K)	H _o (oersted)	Crystal Structure	T _n (K)	Refs.
S2Ta (barium hydrate)0.15	3.74	150	HEX		1845
S ₂ Ta (butylamine)	2.5		HEX	•	1192
S ₂ Ta (butyramide)	3.1		HEX		1192
S2Ta (calcium (0.3) hydrate)	3.47				1770 1845
S2Ta (calcium (0. 15) hydrate)	3.47	130	. HEX		1845
S2Ta (cesium (0.3) hydrate)	2.75, 2.80	110	HEX		1845 1770
S ₂ Ta (cesium hydroxide)	3.8		HEX	,	1192
S2Ta (s-collidine)0.17	2.0, 1.95		HEX		1192 1871
S ₂ Ta (2,6-diaminopyri- dine) _{0.53}	3.50		HEX		1128
S ₂ Ta (2-dimethylamino- pyridine) ₀ , 32	3.15		HEX		1128
S ₂ Ta (4-dimethylamino- pyridine) _{0.34}	2.30		HEX		1128
S2Ta (N, N-dimethylaniline)	4.3		HEX		1192
S ₂ Ta (2,6-dimethlpyri- dine) _{0.20}	2.15		HEX		1128
S2Ta (4,4'-dipyridyl)	2.5		HEX ·		1192
S ₂ Ta (ethylamine)	3.3		HEX		1192
S2Ta (2-ethylpyridine)	3.0		HEX		1128
S2Ta (3-ethylpyridine)0.29	4.50		HEX		1128
S2Ta (4-ethylpyridine)0.33	2.95		HEX		1128
S ₂ Ta (hexanamide)	3.1		HEX		1192
S ₂ Ta (hydrazine)	4.7		HEX		1192
S2Ta (hydrogen)0-0.87	0.8-4.2-<0.5				1871
S ₂ Ta (2-isopropylpyri- dine) _{0.25}	3.80		HEX .		1128
S ₂ Ta (4-isopropylpyri- dine) _{0.28}	2.82		HEX		1128
S2Ta (isoquinoline)	2.5		HEX		1192
S2Ta (lithium hydrate)	3, 83	170	HEX		1845
S2Ta (lithium hydroxide)	4.5		HEX		1192
S2Ta (methylamine)	4.2		HEX '		1192
S2Ta (2-methylpyridine)0.34	2.95		HEX		1128
S2Ta (3-methylpyridine)0.33	2.95		HEX		1128
S2Ta (4-methylpyridine)0.33	2.70		HEX		1128
S2Ta (octadecylamine)	3.0		HEX		1192

TABLE 3 (Cont'd). Properties of Superconductive Materials with Organic and Related Constituents NOTE: "HF" Signifies high-magnetic-field data in Table 5.

Material	T _c (K)	H _o (oersted)	Crystal T _n (K)	Refs.
S2Ta (pentadecylamine)	2.8		HEX	1192
S ₂ Ta (p-phenylenediamine)	3.3		HEX	1192
S ₂ Ta (p-phenylenedia- mine) _{0,25}	2.9		нех	1192
S2Ta (2-phenylpyridine) 0.255	3, 15		HEX	1128
S2Ta (4-phenylpyridine)0.26	1.6		HEX	1128
S2Ta (picoline)0.34	2.70		HEX .	1871
S ₂ Ta (potassium formate)	4.7		HEX	1192
S2Ta (potassium (0, 3) hydrate)	5.25	230	HEX	1845 1770
S ₂ Ta (potassium hydroxide)	5.3		HEX	1192
S ₂ Ta (propylamine)	3.0		HEX	1192
S2Ta (4-propylpyridine)0.25	2.75		HEX	1128
S2Ta (2-propylpyridine)0.245	2.85		HEX	1128
S2Ta (pyridine)0.5	3.5	HF	HEX	1192 1027
S2Ta (pyridine)0.5	3.55		HEX	1128 1871
S2Ta (pyridine) 0.5	3.25	HF .		1262 1430
S2Ta (pyridine-N-oxide)	2.5		HEX	1192
S2Ta (pyridinium chloride)	3.1		HEX	1192
S ₂ Ta (quinoline)	2.8		HEX	1192
S2Ta (rubidium (0.3) hydrate)	4.40	210	HEX	1845 1770
S ₂ Ta (rubidium hydroxide)	4.3		HEX	1192
S2Ta (septadecylamine)	2.7		HEX	1192
S2Ta (sodium (0.3)hydrate)	5.41	250	HEX	1845 1770
S2Ta (sodium hydroxide)	4.8		HEX	1192
S ₂ Ta (stearamide)	3.1, 3.0		HEX	1192
S ₂ Ta (strontium (0.2) ammonium)	2.8		HEX	1918
S ₂ Ta (strontium (0. 15) hydrate)	4.03	190	HEX .	1845
S,Ta (tetradecylamine)	2.4		HEX	1192
S ₂ Ta (N, N, N', N'-tetra- methyl-p-phenylene- diamine)	2.9		нех	1192
S2Ta (thiobenzamide)	3.3		HEX	1192
S2Ta (tributylamine)	3.0		HEX	1192
S2Ta (tributylphosphine)0. 125	2.0		HEX	1192
S ₂ Ta (tridecylamine)	2.5		HEX	1192

TABLE 3 (Cont'd). Properties of Superconductive Materials with Organic and Related Constituents NOTE: "HF" Signifies high-magnetic-field data in Table 5.

Material	T _c (K)	H _o (oersted)	Crystal Structure	T _n (K)	Refs.
S ₂ Ta (2,4,6-trimethyl- pyridine) _{0,165}	1.95	•	HEX		1128
S,Ta (triton B)	5.0		HEX		1192
S, Ta (valeramide)	2.9		HEX		1192
S2Ta0.8W0.2(s-collidine)0.17	2.0		HEX		1192
S2Ta0.3W0.7(s-collidine)0.17				~0.4	1192
S.Ti (ammonia)			HEX	0.3	1192
S ₂ Ti (aniline)			HEX	0.3	1192
S2Ti (s-collidine)0.17			HEX	0.3	1192
S2Ti (pyridine)			HEX	0.3	1192
S2Ti (tributylphosphine)0, 125			HEX	0.3	1192
S ₂ W (strontium (0.2) ammonium)	3.5		HEX		1918
S ₂ W (ytterbium (0.4) ammonium)	2.2		HEX		1918
S ₂ Zr (ammonia)			HEX	0.3	1192
Se ₂ Ta (pyridine) _{0.5}	1.5		HEX		1027
Se ₂ W (strontium (0, 2) ammonium)	~1.4		HEX		1918
V (co-deposited with organic compounds, 50-200Å)	T _c (+~0.1, -~0.1)			1	₹1802

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 P. N. Shelton, and R. E. Schwall, J. Phys. F 4, 2009 (1974).
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- 37. "Detection of Nuclear Quadrupole Resonances via Induced Longitudinal Magnetization," by T. Jach, Appl. Phys. Lett. 28, 49 (1976).
- 38. "Superconductivity and Range of Existence of the A15 Phase in the Nb-Ge Systems," by A. Hallak, R. H. Hammond, R. B. Zubeck, and T. H. Geballe, Bull. Am. Phys. Soc. 21, 340 (1976).
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 J. M. Rowell, and M. R. Beasley, Solid State Commun. 20, 305 (1976).
- 48. "Properties of New Superconducting Materials," Annual Research Progress Report, (November, G. L. Report 2635.
- 49. "Superconducting Materials," by T. H. Geballe, presented at Distinguished Lecture Series III, University of New Mexico, March 1976 (Proceedings in press).

- 50. "Superconductivity Defects and Stoichiometry in Al5 Materials," by R. C. Dynes, J. M. Poate, L. R. Testardi, A. R. Storm, and R. H. Hammond, IEEE Trans. Mag. MAG-13, 640 (1977).
- 51. "Electron-Beam Fabrication of Al5 Superconducting Materials," by
 R. H. Hammond and R. B. Zubeck, presented at American Society
 for Metals Conference on Manufacture of Superconducting Materials,
 Port Chester, New York, November 1976, in press.
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- 53. "Epitaxial Growth of High-T Superconducting Nb₃Ge on Nb₃Ir," by A. H. Dayem, T. H. Geballe, R. B. Zubeck, A. B. Hallak and G. W. Hull, Jr., Appl. Phys. Lett. 30, 541 (1977).
- 54. "Epitaxial Growth of Nb₃Ge on Nb₃Ir and Nb₃Rh," by A. H. Dayem T. H. Geballe, R. B. Zubeck, A. B. Hallak and G. W. Hull, in press.

PERSONS WORKING ON GRANT DURING GRANT PERIOD

Benda, J. A. Ph.D. awarded June 1973

(Thesis title: Optical and Heat Capacity Studies of Some Transition Metal Compounds)

Bilir, N. Ph.D. awarded May 1974

(Thesis title: Low Temperature Heat Capacities of Open-Structured Crystals)

Early, S. R. Ph.D. expected June 1978

Feldman, R. Ph.D. expected June 1980

Hallak, A. B. Ph.D. awarded June 1976

(Thesis title: Superconductivity and Range of Existence of the A15

Phase in the Niobium-Germanium System)

Hammond, R. H. Senior Research Associate

Harper, J. M. E. Ph.D. awarded October 1975

(Thesis title: Thermal Properties of Metals with Low Temperature

Structural Instabilities)

Ierley, G. Received Masters September 1977

Jach, T. J. Ph.D. awarded August 1975

(Thesis title: Observation of Nuclear Quadrupole Resonance

with Superconducting Magnetometers)

Kimhi, D.* Ph.D. expected June 1979

Kwo, J.* Ph.D. expected June 1979

McDavid, G. T. Received Masters April 1974

Meyer, S. F. Ph.D. awarded January 1974

(Thesis title: The Effect of Intercalate and Layer Properties on Superconducting Transition Metal Dichalcogenides)

Moore, D. F.* Ph.D. expected April 1978

O'Connor, M. C. Ph.D. expected June 1978

Pisharody, R. Visiting Research Associate

Phillips, A. W. Visiting Assistant Professor

Salem, J. R. Research Associate

Schwall, R. E. Ph.D. awarded June 1973

(Thesis title: Low Temperature Properties of Layered Transition Metal Dichalcogenide Compounds)

Stewart, G. R. Ph.D. awarded October 1975

(Thesis title: I. Size Effects in the Heat Capacity of Small Metal Particles II. Heat Capacity of the Systems MnBe and MnSb)

Rowell, J. M. Consulting Professor

Younge, R. G. Graduate Research Assistant

Zubeck, R. B. Ph.D. awarded September 1973

(Thesis title: Effects of Deformation on Mixed State Heat Capacity)

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Presentations and Visits During Grant Period

T. H. Geballe

- 10/21/74 SLAC (seminar: "High Temperature Superconductors")
- 11/13/74 UC Berkeley (seminar: "High Temperature Superconductors and Their Applications")
- 11/18/74 Bell Labs (seminar: "Applied Superconductivity: Status and Prospects")
- 4/4/75 CERL, Leatherhead, Surrey, England (visited J. Sutton and discussed use of high-T superconductors in applied technology)
- 5/2/75 Cambridge Univ., England (seminar: "Charge Density Waves in Superconductors and Transition Metal Dichalcogenides")
- 5/9/75 Brown, Bovari Co., Baden, Switzerland (visited A. Menth, discussed superconducting technology)
- 5/14/75 Institute fur Experimentalle Kernphysik, Karlsruhe, Germany
 (visited W. Heinz, discussed synthesis of superconducting compounds using dual beam and sputtering
 techniques; also, new developments of Karlsruhe
 in ion implantation)
- 5/15/75 Siemans, Stuttgard, Germany (visited M. Wilhelm, discussed synthesis of $V_{\rm Q}{\rm Ga}$)
- 5/29/75 A.E.R.E., Harwell, England (visited R. Bett, J. Charlesworth, J. Lee, P. Madsen; discussed Nb₃Sn irradiation damage and manufactur of multifilamentary Nb₃Sn)
- 6/4/75 Imperial College, England (seminar: "Instabilities in Superconductors")
- 7/28-8/1/75 Gordon Conference (chaired session on instabilities in layered dichalcogenides)
- 12/3/75 UC Berkeley (seminar: "Superconducting Power Transmission Lines")
- 2/19/76 UC Santa Cruz (seminar: "Use of Helium and Applied Superconductivity")
- 2/24/76 Bell Laboratories (seminar: "The Superconducting Power Transmission Line")
- 3/4/76 "Distinguished Lecture Series, U New Mexico (Superconductivity: Materials for Energy Use")
- 8/17-20/76 1976 Applied Superconductivity Conference (Conference Chairman

8/14-15/77 International Conference on Physics of Transition Metals, Toronto, Canada

11/14/77 General Motors Research Laboratories, Warren, Michigan (seminar: "Superconductivity in Transition Metals")

J. M. E. Harper

4/7-11/75 IBM, Yorktown Heights, New York

Exxon Research and Engineering Co., Linden, New Jersey

Bell Laboratories, Murray Hill, New Jersey

(seminar: Thermal Properties of Metals with Low Temperature Structural Instabilities)

T. J. Jach IBM, Yorktown Heights, New York

Bell Laboratories, Murray Hill, New Jersey

(seminar: Observation of Nuclear Quadrupole

Resonance with Superconducting

Magnetometers)